MME 231: Lecture 05

# The Laws of Thermodynamics

## The Second Law of Thermodynamics

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# Today's Topics

- The spontaneous or natural processes
- The reversible process
- The second law of thermodynamics and the entropy function
- Intuitive meaning of entropy production
- Entropy and randomness of system

# Introduction

- The First Law of Thermodynamics:

$$\Delta U = Q + W + W'$$

  - **How the values of Q, W and W' be evaluated?**
  - **What magnitudes may the heat and work effects have, and what criteria govern these magnitudes?**

- The answers to these questions require an examination of the nature of processes
  - **which leads to the development of the 2nd law**

- The 1st and the 2nd laws lay the foundation of describing the thermodynamic behaviour of matter.

# Spontaneous Processes

- A process that involves the spontaneous movement of a system from an unstable state to a stable state is called a **spontaneous** process.

  **Example:**

  1. **The mixing of two gases**
  2. **The equalization of temperature**

- All natural processes are spontaneous process.
- This type of process is said to be **irreversible** causing a permanent change in the system.

# Reversible Processes

- The rate of change and the **degree of irreversibility** of a spontaneous process depends on how far the system was from its stable state.
  - **the more distant the system is from its equilibrium, the higher the spontaneity and quicker the rate of change towards equilibrium and the more permanent/ irreversible the change will be.**

- We can imagine a process for which this degree of irreversibility is minimum.
  - **the ultimate lowest limit of this minimisation is a process for which the degree of irreversibility is zero.**

- For this **zero irreversible process**, spontaneity is no longer applicable.
  - **the process passes through a continuum of equilibrium states and the system is never away from equilibrium.**
  - **this type of process is called the reversible process.**

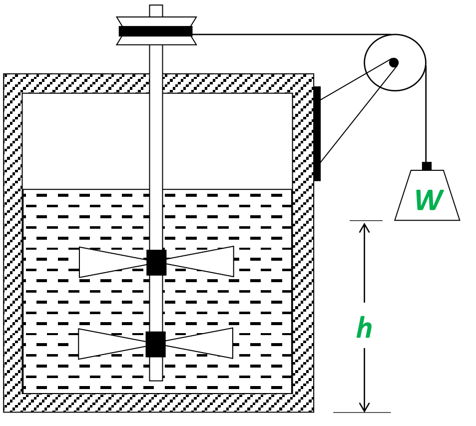
## Consequence of Reversible Process:

- No permanent change in the universe.

## Implication of Reversible Process:

- Although such a path is **imaginary**, it is possible to conduct an actual process in such a manner that it is virtually reversible.
- Since changes in state functions are independent of the process connecting two states, one can always choose the simplest (i.e., a reversible) process, even though the real process is an irreversible one.

# Quantification of irreversibility



1. The heat reservoir in the weight-heat reservoir system is at the $T_2$. The weight is allowed to fall, performing work, and the heat produced enters the reservoir to raise its temperature to $T_3$.
2. The weight-heat reservoir, at temperature $T_2$, is in contact with another heat reservoir at $T_1$ ($<T_2$) and the heat is allowed to flow out to lower the weight-heat reservoir temperature to $T_1$.
3. The heat reservoir in the weight-heat reservoir system is at temperature $T_1$. The weight is allowed to fall, performing work, and the heat produced enters the heat reservoir to raise its temperature to $T_3$.

Process 3, summation of process 1 and 2, is more irreversible than either process 1 or process 2.

- Examination of these processes suggests that the amount of heat produced **Q**, and the temperature **T** at which the heat is produced are important to measure the degree of irreversibility of the process.

- To compare between process 1 and process 3, the quantity

$$Q_1/T_2 < Q_3/T_1$$

which agrees with the conclusion that process 1 is less irreversible than process 3.

**The quantity Q/T is, thus, can be taken as a measure of the degree of irreversibility of the process.**

# The Second Law

- Under a given condition, a system can undergo many processes in which the energy can be conserved (according to the First Law)

- But the processes that occur naturally **have a natural direction of change**.
  - **All of these natural processes occur due to the same cause "some kind of energy in them spreads out."**

- A state function, called **entropy**, is defined to measure the spontaneous dispersion of energy
  - **how much energy is spread out in a process at a specific temperature.**

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- The Second Law is:

There exists a property of the universe, called its **entropy**, which always **tend to change spontaneously** in the same direction no matter what process occurs.

- By convention, entropy is defined so that, when summed for the system and its surroundings, **it always increases**.

- Like the First Law, the Second Law is **general** and **pervasive**, and applies both microscopically to every element of the system or macroscopically to the system as a whole

# The Entropy Function

- Like energy, entropy is a **state function** and an **extensive variable**.
- Unlike energy, entropy can be **transferred** across the boundary of a system as well as can be **produced** inside the system.
- Total change in entropy for the system

$$\Delta S_{sys} = \Delta S_t + \Delta S_p \qquad \textbf{(3.3)}$$

- By second law, for all systems during any process

$$\Delta S_p > 0 \qquad \textbf{(3.4)}$$

- The overall change in entropy for the **universe**, that is, the system plus surroundings:

$$\Delta S_{un} = \Delta S_{sys} + \Delta S_{sur}$$

$$= [\,\Delta S_t + \Delta S_p\,] + [\,\Delta S'_t + \Delta S'_p\,]$$

$$\Delta S_{un} = \Delta S_p + \Delta S'_p > 0 \qquad \textbf{(3.6)}$$

- Thus, for any kind of process,
**the entropy of the universe can only increase**.

# Intuitive Meaning of Entropy Production

- Changes in real world are always accompanied by friction, and some energy is dissipated.
  - **Entropy production is quantitative measure of this dissipation of energy**
  - **The further a system is from its equilibrium state, the faster it tends to change, the greater the frictional or dissipative effects, and the larger its rate of entropy production**

- Entropy and cause some **permanent change** in the universe.
- Total entropy change of the universe always increases due to spontaneous change with increasing time.
- Reversible processes occur very slowly, suffer least dissipation, and have **zero entropy production**.

- The first law deals with the **conservation of energy,** but the second deals with the **degradation of energy**.
  - **The production of entropy term accounts for this degradation of energy**

## Entropy vs. Randomness

- Considering **the** atomic scale, Gibbs relates entropy of a system to the degree of **mixed-up-ness** of the system.

- More mixed up (or, random) the constituent particles of a system is, the larger the value of its entropy.
  - **Crystalline solids have regular arrangement of atoms in a rigid framework and, thus have lesser entropies.**
  - **The atomic disorder in the gaseous state is the maximum, and so is the value of its entropy.**

## Next Class

**Lecture 06**

**The Second Law of Thermodynamics ...**

**Rashid/ Ch#3 – Sec. 3.2**